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CHEMICAL BIOLOGICAL CENTER

U.S. ARMY SOLDIER AND BIOLOGICAL CHEMICAL COMMAND

ECBC-TR-293

CHEMICAL CHARACTERIZATION
OF THE PYROTECHNICALLY DISSEMINATED
M8-PE SMOKE POTS

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To reduce the possibility of flaming, the smoke formulation for the M8 smoke pot has bee n modified by the addition of a burn retardant, penterythritol (PE). These M8-PE pots were chemically characterized to qualitatively and quantitatively determine the combustion products produced with the addition of PE. Data as needed prior to material release and for incorporation into the item's Life Cycle Environmental Assessment (LCEA). Similar to other terephthalic acid (TA) based smokes, benzene, formaldehyde, and carbon monoxide were the principal compounds observed of toxicological concern. A comparison is made between the M8-PE smoke pots and M8 pots, which shows that benzene appears to be lower in the PE pots; but, formaldehyde appears to be higher. All concentrations exceed the currently accepted American Conference of Government Industrial Hygienists (ACGIH) Threshold Limit Values (TLV'S). Carbon monoxide levels are also much less in the PE pots, but were above the ACGIH TLV's. Other inorganic gas concentrations, such as nitrogen oxides and sulfur oxides, were determined, but comparisons were not made to the M8 smoke pots. Particle size analysis was conduced for the M8-PE pots with the observance of small diameter particles (1-2 μm).

14. SUBJECT TERMS

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PREFACE

QUALITY ASSURANCE

The report of this study, titled "Chemical Characterization of the Pyrotechnically Disseminated M8-PE Smoke Pots", was examined for compliance with Good Laboratory Practices as published by the U. S. Environmental Protection Agency in 40 CFR Part 792 (effective 17 Aug 1989). The date of this inspection and the dates the results were reported to the Study Director and management were as follows:

Phase Inspected	Date	Date Reported
Data and Final Report	21 Oct 02	21 Oct 02

To the best of my knowledge, the methods described were the methods followed during the study. The report was determined to be an accurate reflection of the raw data obtained.

DENNIS W. JOHNSON   29 Oct 02
Quality Assurance Coordinator
Toxicology, Aerosol Sciences and
      Obscurants Senior Team
Research and Technology Directorate

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CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED M8-PE SMOKE POTS

1.   INTRODUCTION

Historically, the use of smokes and obscurants has been important to the military in both combat and training situations. Hexachloroethane (HC) grenades and smoke pots were once used for training purposes due to their excellent obscuration qualities. However, they were later observed to produce hazardous combustion products of toxicological concern.[1] Terephthalic acid (TA) emerged as the new fill component for smoke grenades and pots due to its less toxic nature based on the current American Conference of Government Industrial Hygienists (ACGIH) recommended limits.[2,3] Threshold Limit Values (TLV's) are listed for known hazardous substances and represent the concentrations that workers may be exposed to daily without experiencing health effects. The three subcategories of TLV's listed are Threshold Limit Value-Time Weighted Average (TLV-TWA), Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) and Threshold Limit Value-Ceiling (TLC-C).[4] These represent the various exposure conditions and durations that may occur. The M83 smoke grenade and M8 smoke pot are two hardware configurations that utilize terepthalic acid formulations. Chemical characterizations have been performed for these items with analyses showing benzene and formaldehyde concentrations to be at or above their respective TLV's.[3] Still, these formulations are considered to be the least toxic smoke grenades available to the military for training purposes.

With a continued thrust to reduce potential hazards associated with the M8 pots, a research effort has been initiated to address the high temperature flaming occurrences that sometimes occur among these hardware items. Modification of the smoke formulation was performed to create a slower burn, and therefore greatly reduce the possibility of a flame hazard. Experiments confirmed that when pentaerythritol (PE) was added to the TA smoke formulation, it served as a burn rate retardant.[5] Although retardants normally reduce the smoke yield, the performance of the M8-PE pots was not compromised because the PE is a smoke-producing component itself.

The addition of a new component to the existing formulation has required a new Health Hazard Assessment (HHA) to be performed before Material Release of the item may be granted. A new HHA is also required for differing hardware configurations of the same smoke composition. Paramount to this is a chemical characterization to determine what effect the modified formulation and burn rate have on the combustion products produced. Comparisons may therefore be made to determine whether increased risks occur through higher concentrations of toxic substances.

2.   MATERIALS AND METHODS

2.1   Materials – M8-PE Pots.

The M8-PE pots (Lot # PB01B041A001) were transported from Pine Bluff Arsenal (PBA) to the Edgewood Chemical and Biological Center's (ECBC) Engineering Directorate for storage. On days of testing, the pots were delivered downrange to a designated field testing site. The hardware design of the pot is the same as for the M8 pots, but the starting smoke formulation is different. The composition of the M8-PE and M8 smoke mix are provided in Table 1. Within the mix, 33% of the TA from the original M83 smoke formulation has been replaced with PE. The weight of the smoke mix batch was 499 kg and was prepared by Pine Bluff Arsenal (PBA) on February 26, 2001. No discernible differences were present between the starter mixes of the two pots.

2.2   Field Testing Experimental Design.

All smoke pots were disseminated on a concrete slab. To trap the smoke a 6' x 6' x 10' wooden shed was constructed (Figure 1) with an 8' plywood tunnel attached to the open end. The pot was placed on the concrete approximately one foot deep inside the tunnel to reduce dissipation of smoke away from the shed. After the pin was broken, smoke was expelled from the pot and forced to travel down the tunnel into the shed (Figure 2). Normally, one minute was required to fill the shed with smoke. Although there was no space for the smoke to exit, the study was designed to simulate static conditions inside the shed. The option for performing a dynamic test in a closed environment as for other smaller smoke items does not exist for the larger pots.

High smoke concentrations were produced for a sufficient quantity of time to allow characterization of the smoke. Samples were collected on wooden tables in the shed about 4 feet above the ground, and about 8 feet from the pot. Meteorological conditions were monitored on sampling days.

2.3   Shed Concentration.

To monitor the total aerosol concentration in the shed, 25 mm A/E glass fiber filter pads (Gelman Scientific) were used to collect particulate samples. Flow rates varied according to the amount of smoke produced by an individual pot. Initially, it was unknown what volumes of air should be drawn to obtain a measurable mass of material on the pad without overloading it. Therefore 1 L of air was drawn from pot 1 (2 min @ 0.5 L/min) and 2 L of air were drawn from pot 2 (4 min @ 0.5 L/min) before deciding that 0.5 L of air drawn worked well for the experiments. For pots 3-10, 0.5 L of air (1 min @ 0.5 L/min) were drawn from the shed onto the pads using a calibrated vacuum pump (Sierra Instruments). Sampling began once the shed was filled with smoke. This time varied because not all pots filled the shed at an equivalent rate. Gravimetric analysis was performed on the resulting pads using a Cahn microbalance to determine the total aerosol concentrations.

2.4   Particle Size Analysis.

A 10-stage cascade impactor (Sierra Instruments) was used to monitor particle size distribution. For each pot, air was drawn from the shed through the impactor for 0.5 min @ 7 L/min. The start time corresponded to the time at which the shed concentration was measured. To avoid overloading or clogging the impactor, the total weight collected among all the pads was kept under 10 mg.

2.5   Chemical Characterization.

Sampling collection devices were affixed to 3' x 3' square boards at the entrance to the shed. The boards were placed on a four-foot high table in the middle of the shed to collect representative samples of the smoke cloud.

2.5.1   Volatile Organic Combustion Products (VOC's).

As shown in Figure 3, VOC's of the combusted smoke were collected with four separate 20:35 mesh tenax TA tubes (Dynatherm Inc. Part Number MX0621112035). Due to the high aerosol concentration in the shed, 25 mm A/E glass fiber filter pads were attached to the entrance of each tube to prevent aerosols from collecting in the tubes. Samples were collected for 1 min @ 25 mL/min with a Sierra vacuum pump, refrigerated, and subsequently analyzed by thermal desorption gas chromatography mass spectrometry (GC/MS). To adjust for any resistance, flows were set with the pads attached to the tubes. Rates were set with valves and rotameters and checked against an external flow-measuring device (Drycal).

Quantitative analysis was performed on compounds of toxicological concern. Gastight syringes (Hamilton) were used to draw predetermined gas volumes from aerosol cans (Scott Specialty Gas) containing a known concentration of analyte in air. The analyte was injected onto a tenax tube and swept onto the sorbent with a low flow of nitrogen (<50 mL/min). A minimum of four standards were injected with a correlation coefficient (r^2) > 0.99. All sampling and analysis procedures described were in accordance with the NIOSH approved screening method.[6] The thermal desorption GC/MS conditions are shown in Appendix A.

2.5.2   Formaldehyde Analysis.

On the same 3' x 3' board used to take VOC samples, air samples were drawn for 2 min @ 1 L/min onto two separate tubes for formaldehyde analysis (Figure 3). Again, glass fiber filter pads were attached to the entrance of each tube to prevent aerosol collection. 2,4 dinitrophenylhydrazine cartridges (LpDNPH) from Supelco Inc (Cat no. 21014) were used to trap formaldehyde onto a high purity silica absorbent. Using gravity feed, the cartridges were eluted with approximately 5 mL of acetonitrile and prepared for gas chromatography flame ionization (GC-FID) analysis (Appendix B for instrument conditions). This method has proven reliable in the analysis of formaldehyde and other longer chain carbonyl compounds.[7] Concentrations were also measured with compound specific detector tubes as described in Section 2.5.3.

2.5.3   Inorganic Analysis.

        Although large quantities of soot were observed from dissemination of the smoke pots, the solid "fallout" material was not collected or analyzed during this study. On a separate 3' x 3' wooden sheet, three glass cylinders with filter pads at each entrance were attached for inorganic gas sampling. Electronic solenoids were used to open and close the cylinders. Samples were taken for two minutes using a constant flow vacuum pump. The contents of the cylinders were transferred to a separate 4.5 L Teflon gas sampling bag (Alltech) with a 2 L gastight syringe for the determination of carbon monoxide, carbon dioxide, sulfur oxide, and nitrogen oxide concentrations. Further air dilution was necessary to achieve a sufficient volume to perform analyses for all the inorganic gases.

        According to the air volumes predetermined by the manufacturer, samples were pulled from the bag onto a compound specific detector tube using a Matheson portable gas sampling pump (Model 400). Concentrations were recorded by monitoring the colorimetric change observed on the sorbent material.

3.   RESULTS

3.1   M8-PE Disseminated Smoke Pots.

        Burn times for the smoke pots were visually observed and are recorded in Figure 5. To account for the slight delay on pulling of the pin, the start time was defined as the time when smoke was initially produced. The average burn time over the ten smoke pots was 276 ± 29 sec.

3.2   Shed Concentration.

        Figure 6 shows the total aerosol concentrations present in the shed during times of sampling. Due to a lack of strict experimental controls for maintaining a constant concentration, the coefficient of variation (45.6 %) is considerably higher than what would be expected in a contained chamber system. For the 10 pots, the mean concentration was 4835 ± 2207 mg/m.^{3}

3.3   Particle Size.

        Particle size was calculated from seven of the ten smoke pots. A different particle size instrument was used during pots 1 and 2, but it's design made it ineffective for the study. For pot 3, the total quantity of smoke material collected among all of the stages was too low (2 mg) to conduct analysis. The mean concentration at which particle size was recorded was 5413 ± 2189 mg/m^3 (C.V. = 40.0%). The mass median aerodynamic diameter (MMAD), geometric standard deviation (σ_g), and respirable mass percentage are all presented in Table 2.

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3.4   Chemical Characterization.

3.4.1   Volatile Organic Combustion Products (VOC's).

Volatile organic combustion products were collected from the shed for subsequent analyses. Tubes for the first pot could not be analyzed because the flow rates were set higher than for the other pots. Accurate quantitation would not be possible due to overloading of the detector. Benzene was the only compound trapped that exhibited any significant concentration levels. Figure 7 shows the concentrations calculated for each of the tubes collected. On two of the pots, a different sorbent other than tenax (carboxen) was used to determine if it possessed higher collection efficiency for the compounds of interest. Subsequent analysis showed that tenax was a more superior sorbent. In addition, one pot had the samples lost during transfer from two of its collected tubes. After combining all data (n= 28), the concentration of benzene produced by dissemination of these pots was 49 ± 24 ppm. Variability may be attributed to the wide differences in total aerosol concentrations collected in the shed. Strict control on uniformity throughout the shed was not possible in the described methodology. All values exceed the Threshold Limit Value (TLV) established by the ACGIH (Table 3). The current TLV-TWA for benzene is 0.5 ppm and the TLV-STEL is 2.5 ppm.

3.4.2   Formaldehyde Analysis.

For each smoke pot, Table 3 lists the formaldehyde concentrations (GC analyses) at a distance of eight feet from the pot. In combining all the data, the concentration of formaldehyde produced by dissemination of these pots is 50 ± 20 ppm. All values exceed the Threshold Limit Value (TLV) established by the ACGIH. The current TLV-C for formaldehyde is 0.3 ppm.

3.4.3   Inorganic Analysis.

Table 4 lists the inorganic gas concentrations observed for each grenade. The mean concentrations for all runs are also presented with their corresponding standard deviations. TLV-TWA values for each of the inorganic gases analyzed are also shown. Although sulfur oxide gases were measured, there were many instances where the colorimetric limit of detection was not reached on the tubes. Therefore a worst-case concentration was calculated to correspond with the limits of the detector tube (0.5 ppm). The average SO_x concentration reported for each pot and the combined average reported for all of the pots will therefore be higher than the actual values. For pot 4, all SO_x readings were higher than the other pots. The other inorganic gases measured did not reflect any large differences from the mean. Therefore, no explanation may be reached concerning these elevated SO_x readings. Exclusion of this data from the overall average was justified by using the Grubb's test (External Studentized Test) for detection of outliers. Several tubes were also collected and analyzed for nitrogen oxide compounds.

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4.   DISCUSSION

When the smoke composition is altered for an existing type-classified formulation, it is important to perform a new chemical characterization of the combustion products. Data are necessary to perform a new HHA before material release of the item. Results have been collected on the dissemination of this formulation from the grenades, but questions arise whether the differences seen in combustion products between the grenades and pots is altered through dissemination of a greater amount of material and in a different manner. Pentaerythritol has been added as a burn retardant in order to make the M8-PE smoke pots safer items through eliminating the possibility of a flame hazard. The formulation shown in Table 1 was determined to be the optimal mixture of TA and PE without sacrificing obscuration yield.

Comparisons may be made between the chemical characterizations performed on the M8-PE smoke pots with previous work performed by Anthony, et.al. on the M8 pots.[8] Changing trends may be identified on the addition of the burn retardant, but there are several reasons why quantitation of differences is not possible. First, the analytical methodology for determining benzene and formaldehyde concentrations has improved from the earlier study. Secondly, combustion product concentrations can fluctuate as the concentration of total aerosol in the shed fluctuates. This caused wider standard deviations to be seen in the combustion product concentrations because there are no strict controls possible on the experimental design.

Table 5 shows some of the trends in combustion product differences between the two pots. Benzene concentrations decrease by nearly 25% from the M8 to the M8-PE pots. Both concentrations are representative of samples taken from the shed at a distance of 8 feet from the dissemination source. This same trend has been seen in the M83 and M83-PE grenades in that the benzene concentrations dropped nearly 50% in moving to the PE grenades.[8] In the current study, experimental design did not allow for engineering controls to be utilized to maintain a constant concentration. Therefore, the aerosol concentration differences are greater in the M8-PE pots than in the M83-PE grenades.

Formaldehyde concentrations increase about 30% from the M8 to the M8-PE pots. Samples are representative of samples taken from the shed at a distance of 8 feet from the dissemination source. Formaldehyde concentrations also increased in the M83-PE grenades by approximately 40%.

The increased levels of formaldehyde could be explained from how it is produced. Pentaerythritol is formed through an aldol condensation reaction between acetaldehyde and formaldehyde, followed by a Cannizzaro reaction.[9] In PE combustion, the possibility could exist where a reverse aldol reaction occurs and releases additional formaldehyde as compared to the M83 grenades without PE. Higher concentrations of formaldehyde could cause lower total concentrations of other combustion products, namely benzene.

The MSDS for pentaerythritol states that hazardous decomposition products are toxic fumes of carbon monoxide and carbon dioxide, but only increased levels of carbon dioxide were observed between the M8 and M8-PE pot.[10] This observation was not made in the respective M83 and M83-PE grenades. Carbon monoxide levels were dramatically decreased

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between the two pots. This trend was also seen in the respective grenades at a lower magnitude. Sulfur oxide and nitrogen oxide concentrations were not measured from the M8 smoke pots, and therefore, no comparisons or trends may be made with the current M8-PE pots. As a worst case, sulfur oxide concentrations appear to be nearly two times greater than the allowable TLV-TWA, and nitrogen oxide concentrations were negligable.

Analysis of the particle size data between the M8-PE and M8 pots illustrate similar results. Both have MMAD's less than 3μm, indicating that a majority of the particles are respirable and can be deposited deep into the lung. Typically, all particles less than 5μm will follow this deposition pattern.[11]

5.   CONCLUSIONS

Pentaerythritol was introduced to the M8 TA based training pots to act as a burn retardant and reduce flaming hazards associated with them. Many of the same combustion products were seen, but some of their concentrations levels had changed. This could be caused by the differing burning temperatures or by less total aerosol produced.

Analysis was performed on data collected from pyrotechnically disseminated M83-PE smoke pots. Benzene, formaldehyde, and carbon monoxide were all present in concentrations above their respective TLV-TWA's. In comparison to the M8 pots, benzene concentrations decreased by nearly 25%, formaldehyde concentrations increased by nearly 30%, and carbon monoxide levels decreased nearly 300%. Carbon dioxide levels were much higher than the M8 pots but were still below established exposure limits. Sulfur oxide and nitrogen oxide concentrations were not measured for the M8 pot and therefore no comparisons could be made. Particle size distribution revealed the presence of respirable particles with MMAD's of 1-2 μm.

The TA based formulations still appear to produce the least toxic smokes for military use. Although some combustion product concentrations have been changed, there were no additional products seen. None of the grenades flamed during the test.
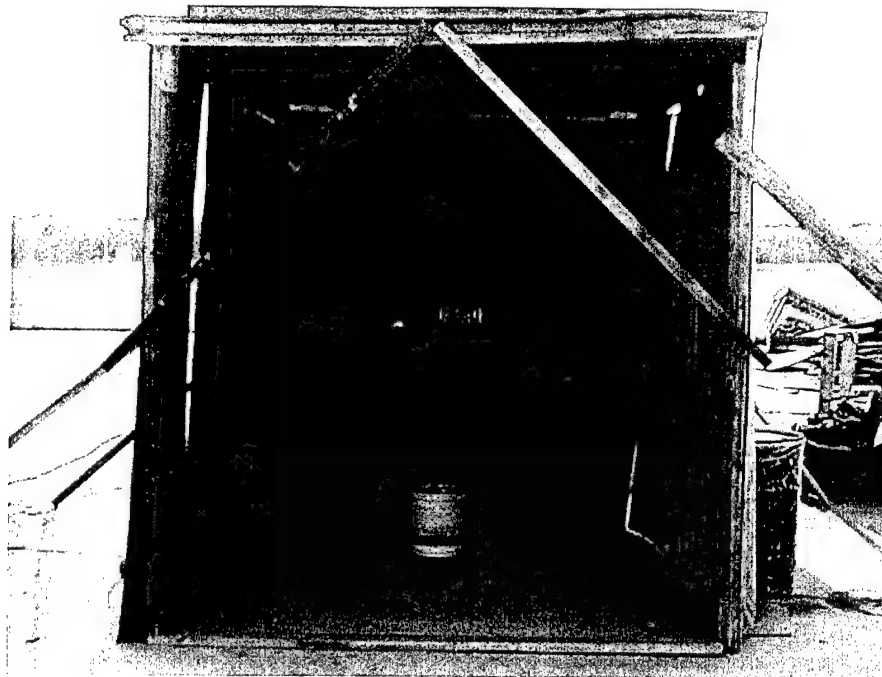
Figure 1 – Field setup for dissemination of M8-PE smoke pot

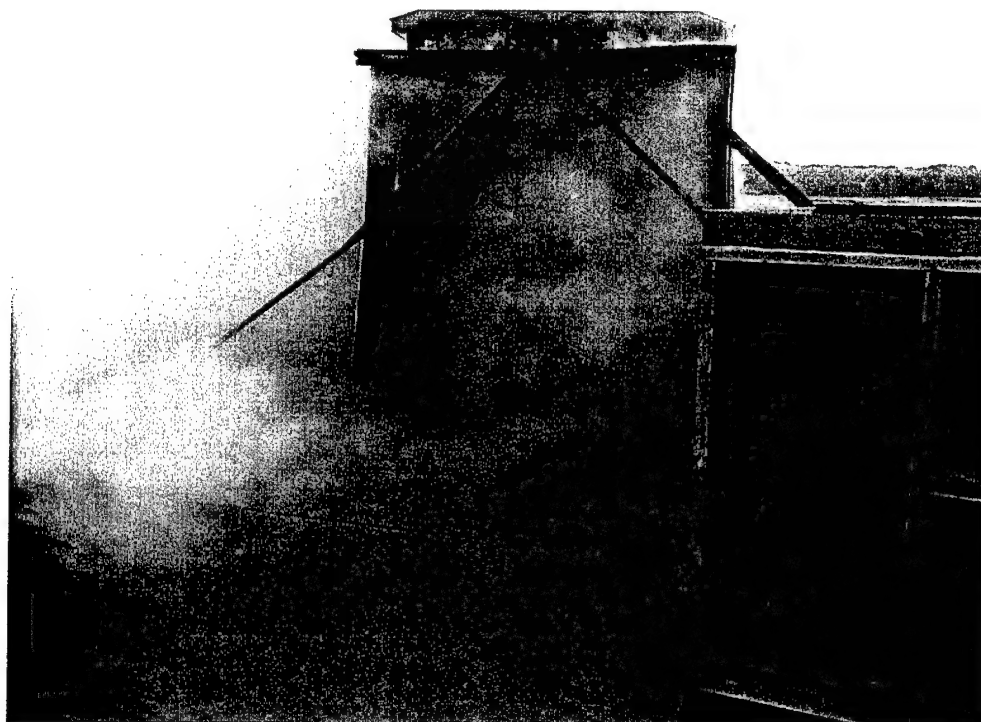Figure 2 – Smoke production from dissemination of M8-PE smoke pot
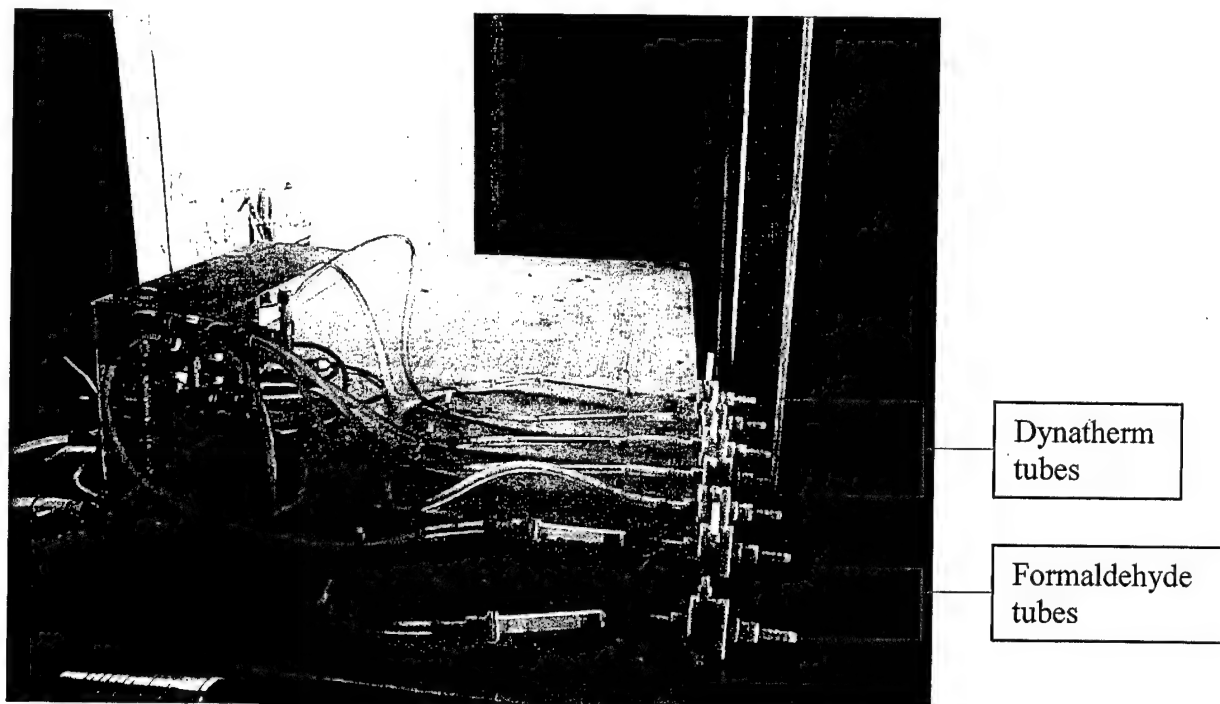
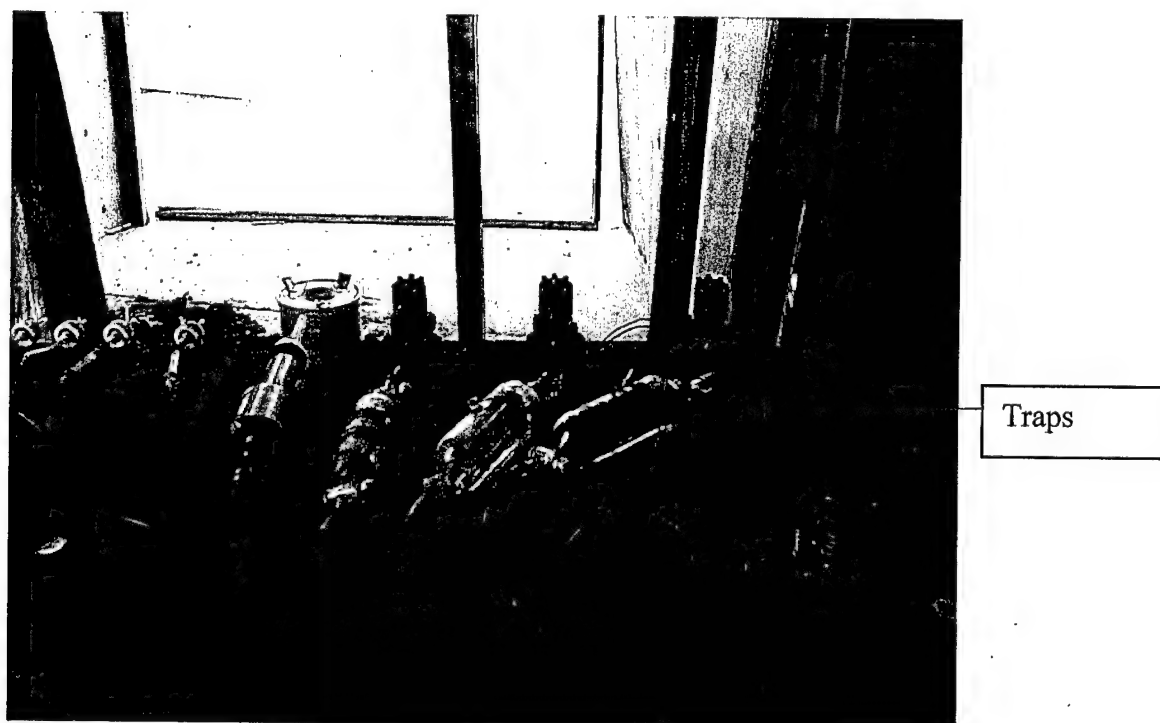Figure 3- Sampling apparatus for benzene and other volatile organics

Figure 4 – Glass cylinder traps for inorganic gas collection and cascade impactor for particle size distribution

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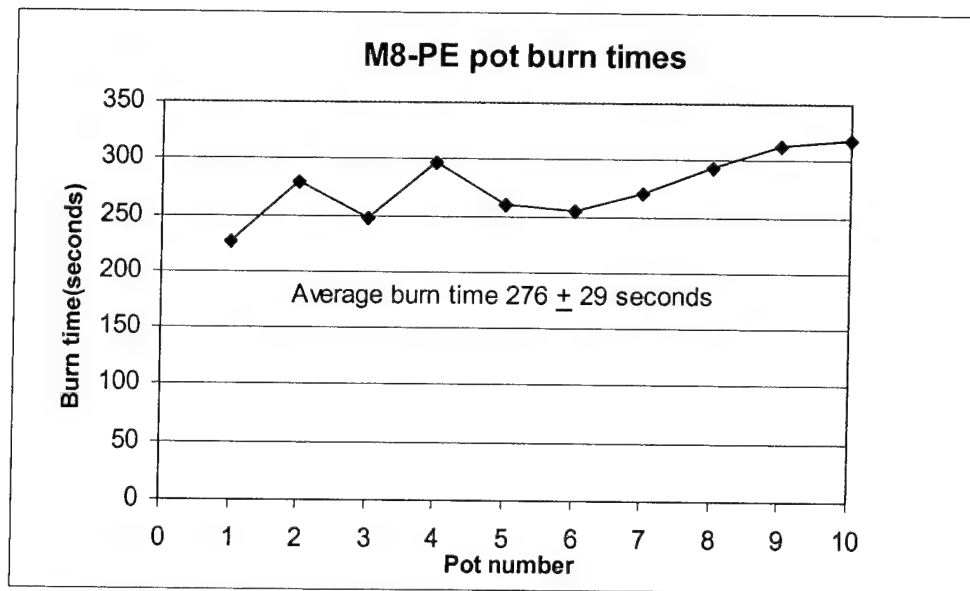
Figure 5 – Burn times for the M8-PE pots
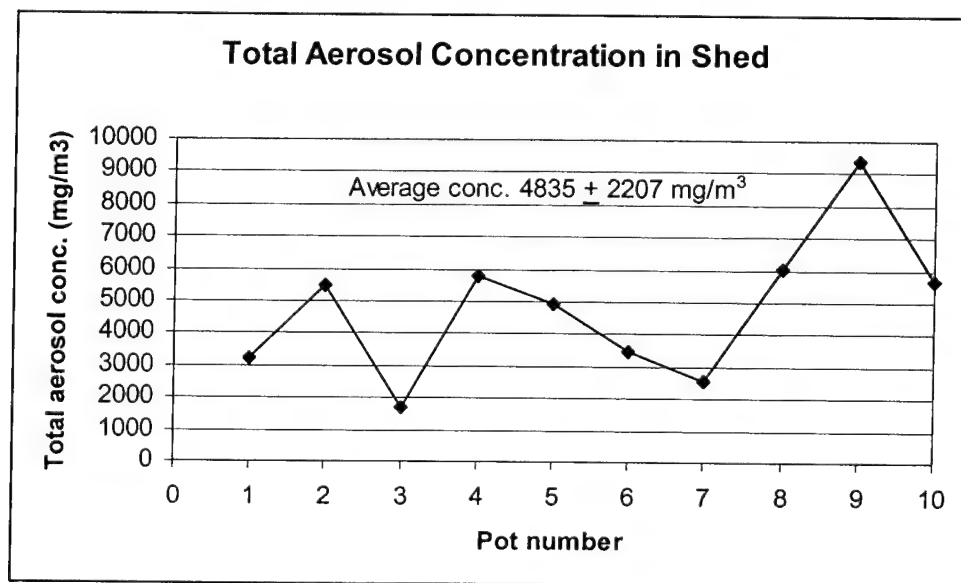
Figure 6 – Total aerosol concentration in the shed (mg/m³)
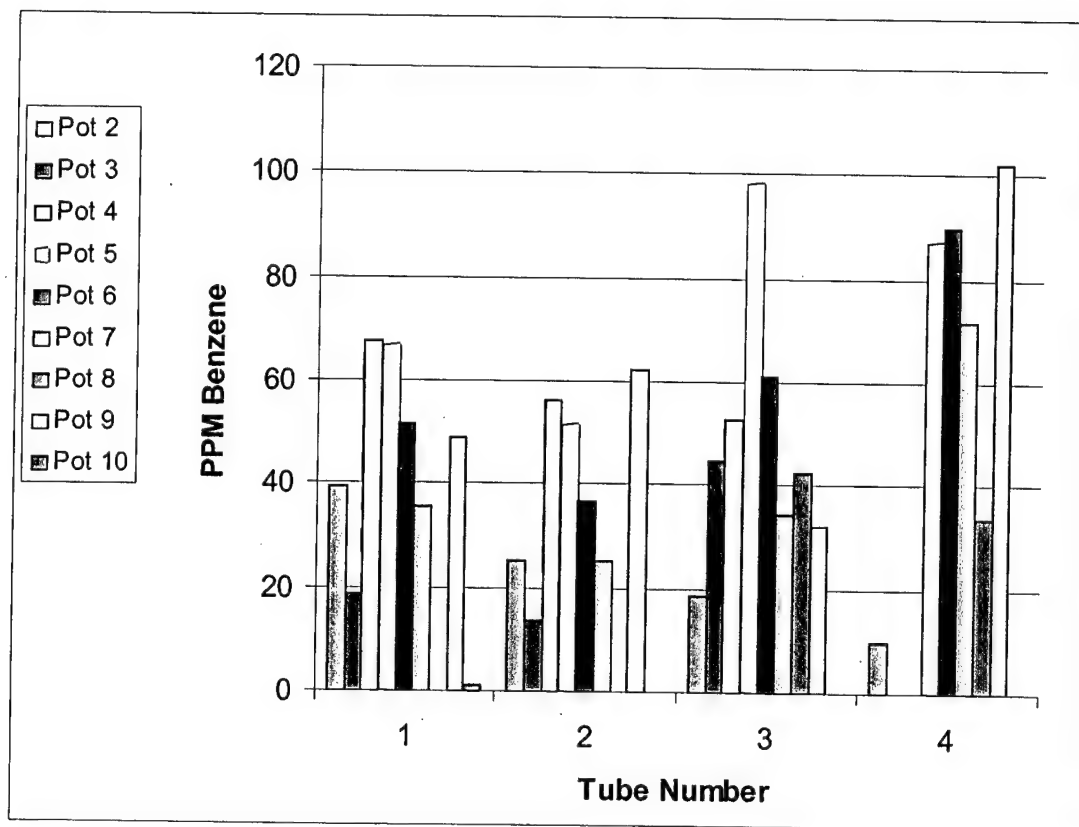
Figure 7 – Benzene concentrations in the shed

Table 1. M8-PE and M8 Smoke Formulations

Material	*M8-PE	*M8	
Terephthalic acid	36.26	56.4	*98% of the total fill weight
Pentaerythritol	17.91	0	
Sugar	13.64	13.9	
Magnesium carbonate	7.55	3.0	
Sodium bicarbonate	1.18	0	
Potassium chlorate	22.36	22.8	
Stearic acid	1.00	3	
Binder	0.75	1	

Table 2. *Particle Size Analysis

MMAD (μm)	2.1 ± 0.5
σ_g	1.5 ± 0.08
Respirable Mass (%)	82.7 ± 7.1

*Data presented as the average of pots 4-10

Table 3. Concentrations of VOC's Measured in M83-PE Grenades

Pot	[a]Benzene		[b]Formaldehyde	
	[a]Conc. (ppm)	St. Dev.	[a]Conc.(ppm)	St. Dev.
2 (n=4)	**23**	12	**23.5**	0.7
3(n=3)	**26**	17	**33.5**	0.7
4(n=3)	**59**	8	**39.0**	2.8
5(n=4)	**72**	24	**83.5**	4.9
6(n=4)	**50**	12	**41.0**	1.4
7(n=4)	**32**	6	**36.0**	1.4
8(n=4)	**54**	26	**52.5**	6.4
9(n=2)	**61**	30	**64.0**	1.4
10(n=)	**10.0**	1.4	**73.5**	3.5
Average 2-	**49.0**	24	**50**	20

[a] TLV-TWA for benzene is 0.5 ppm and the TLV-STEL is 2.5 ppm as established by the ACGIH 2002.
[b] TLV-C for formaldehyde is 0.3 ppm as established by the ACGIH 2002, GC analysis
Values above their TLV (TWA) are in bold

Table 4 . Inorganic Gas Combustion Products Measured Using Matheson Gas
Detector Tubes

Pot	[b]CO [a]Conc.(ppm)	[c]CO$_2$ [a]Conc.(ppm)	[d]SO$_x$ [a]Conc.(ppm)	Formaldehyde [a]Conc.(ppm)
1	**265**	4420	**4.0**	57
2	**470**	4452	**4.0**	61
3	**216**	3300	**4.1**	66
4	**256**	3260	**outlier**	101
5	**118**	3300	**3.0**	57
6	**112**	2680	**3.6**	28
7	**184**	3200	**3.0**	66
8	**152**	2780	**3.6**	15
9	**334**	4260	**3.6**	34
10	**184**	3040	**3.6**	39
Avg 1-10	**229 ± 114**	3469 ± 1016	**3.6 ± 0.4**	51 ± 24

[a]Values are the means of concentrations recorded for the three glass cylinders.
[b] TLV-TWA for carbon monoxide is 25 ppm as established by the ACGIH 2002.
[c]TLV-TWA for carbon dioxide is 5000 ppm as established by the ACGIH 2002.
[d] TLV-TWA for sulfur dioxide is 2 ppm as established by the ACGIH 2002.
Values above their TLV -TWA are in bold

Table 5. Benzene and Formaldehyde Comparisons Between
the M8-PE and M8 Smoke Pots

	M8-PE smoke pot	*M8 smoke pot
Total aerosol conc. (mg/m^3) [Benzene conc. (ppm)]	4835 ± 2207 49 ± 24	8014 ± 2331 63 ± 14
Total aerosol conc. (mg/m^3) [Formaldehyde conc. (ppm)]	4835 ± 2207 50 ± 20	8014 ± 2331 34 ± 7

* Data from Anthony et al (1995)

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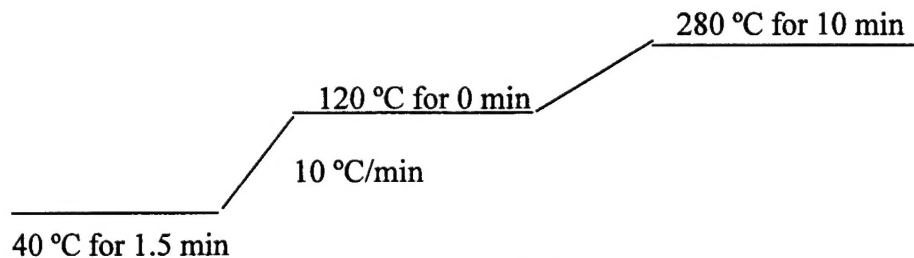
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APPENDIX A

THERMAL DESORPTION GC/MS CONDITIONS

<u>Thermal Desorption Conditions</u>

Instrument: Dynatherm ACEM900 Thermal Desorption Unit

Valve temp:	150 °C	Dry time:	1 min
Tube temp:	250 °C	Tube heat:	3 min
Transfer line temp:	200 °C	Tube cool:	1 min
Trap temp:	250 °C	Trap heat:	3 min

<u>GC Conditions</u>

Instrument: HP 6890 Gas Chromatograph
Column: HP-5MS 30m x 0.25mm x 0.25 μm
Column Flow(He):   1.0 mL/min (velocity 36 mL/min, head pres 7.06 psi)

Temperature program

280 °C for 10 min

120 °C for 0 min

10 °C/min

40 °C for 1.5 min

<u>Detector Conditions</u>

Detector: HP5973 mass selective detector
MS quad temp: 150 °C
MS source temp: 230 °C
Scan parameters: 30-550 amu; threshold 150

Blank

APPENDIX B

GC/FID CONDITIONS

Instrument: HP 5890 Gas Chromatograph
Column: J+W Scientific DB-5 30m x 0.53mm x 1.5μm
Liner: Single Taper (HP part number 5181-3316)
Injection volume: 2 μL splitless
Column flow(He):   1.0 mL/min (velocity 36 mL/min, head press = 8.5 psi

Inlet purge: Off time: 0 min; On time: 0.5min
Injector temp: 220 ºC

Temperature program   15 min @ 300 ºC

             10 ºC/min

     2 min @150 ºC

                         Detector Conditions

Detector: Flame ionization detector
Detector temp: 300 ºC
Detector flow: 400 mL/min (air); 30 mL/min (hydrogen)